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A Phased Approach for Characterization of Multimedia Discharges from Processes

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16. ABSTRACT

This paper discusses a phased approach for characterization of multimedia discharges from industrial and energy processes. In a phased approach, as opposed to a direct approach, all streams are first surveyed using simplified, generalized sampling and analytical methods which permit the streams to be hazard-ranked. Detailed sampling and analysis is then applied first to streams ranked in the highest priority by the survey, and then to other streams in descending order of potential hazard. Another phase, initiated after complete characterization of potential problems, involves continuous monitoring of key indicator materials to evaluate long-term process variability. The phased approach has been sucessfully implemented on many programs. Level 1 results have been useful for defining potential problems for further study and directing additional resources into the areas of greatest need. While not all the elements have been effective on each study, every element has produced needed data in at least one individual study. In considering the utility of the approach it is therefore necessary to consider the overall results. The procedures selected initially have been constantly improved in detail; however, no significant changes in the basic techniques have been necessary. The phased approach is, therefore, a viable and cost effective concept for identifying potential environmental problems associated with discharge from industrial and energy processes.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Assessments	Stationary Sources	14B
Properties	Environmental Assessment	
Industrial Processes	Phased Approach	13H
Sampling		
Analyzing		
Toxicity		06T

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A Phased Approach for Characterization of Multimedia Discharges from Processes

J. A. DORSEY, L. D. JOHNSON, and R. G. MERRILL

Industrial Environmental Research Laboratory, Environmental Protection Agency, Research Triangle Park, NC 27711

In recent years, concern for the environmental impact of discharges from industrial and energy processes to air, water, and land receptors has expanded far beyond the traditional lists of a few selected pollutants. This has given rise to the concept of a comprehensive characterization of all materials released to the environment, and the phrase "environmental assessment" has been added to the vocabulary of many organizations. The four major components of an environmental assessment, as used by our group, are as follows: *(1)*

1. A systematic evaluation of the physical, chemical, and biological characteristics of all input and output streams associated with a process;
2. Predictions of the probable effects of those streams on the environment;
3. Prioritization of those streams relative to their individual hazard potential; and
4. Identification of any necessary pollution control technology programs.

This process is depicted schematically in Figure 1.

It is obvious that such an assessment is formidable, technically difficult, and extremely expensive. Since an environmental source assessment study is required to characterize the total pollution potential of all waste streams, the sampling program must be more extensive than those conducted for the acquisition of process or control engineering data. Assessment sampling is more complete in that all waste streams are sampled and no attempt is made to limit sampling to a preselected number of process streams. The sampling is also more comprehensive in that all substances of potential environmental concern must be detectable above some minimum level of concern. These requiements of completeness and comprehensiveness call for a strategy of approach in which the philosophy and structure ensure maximum utilization of available resources.

Approach

Two clearly distinct strategies to an environmental assessment sampling and analysis program that satisfy the requirements for comprehensive information are the direct and phased approaches. In a direct approach, all streams would be carefully sampled and the samples subjected to complete, detailed analysis using compound specific analytical techniques. In a phased approach, all streams would first be sur-

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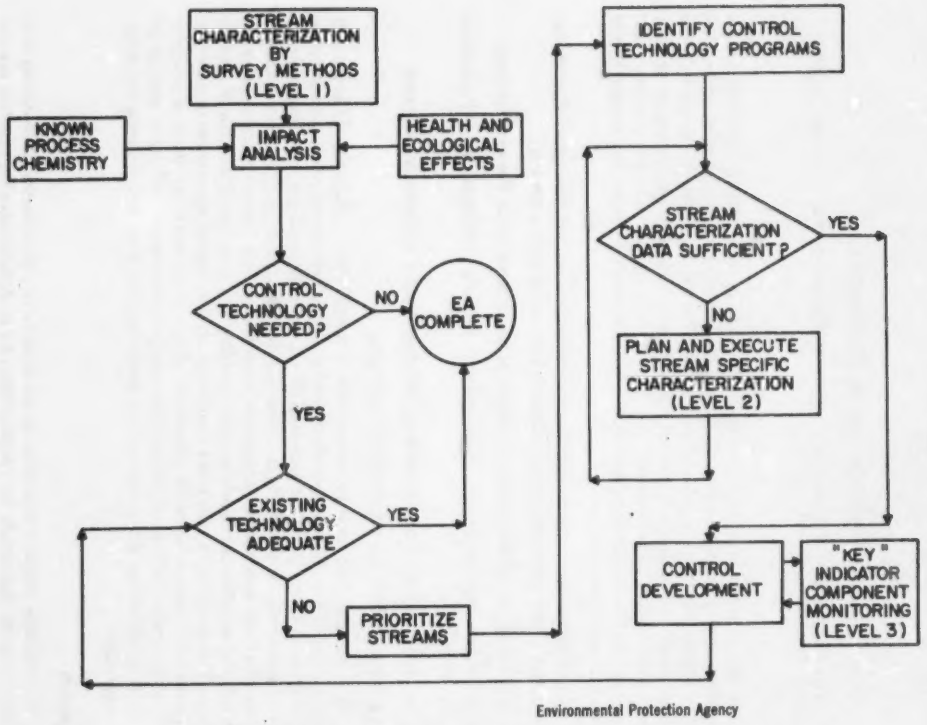

Figure 1. Flowchart of an environmental assessment process (1)

veyed using simplified, generalized sampling and analytical methods which would permit the streams to be ranked on a priority basis; i.e., very hazardous streams would be distinguished from those less hazardous or relatively innocuous. Detailed sampling and analysis would then be applied first to streams ranked in the highest priority by the survey, and then to other streams in descending order of potential hazard. Another phase, initiated after complete characterization of potential problems, would involve continuous monitoring of "key" indicator materials to evaluate long-term process variability.

It should be clear that any partially direct approach (e.g., the use of predetermined lists of compounds) is not consistent with the complete and comprehensive requirements of either the direct or the phased environmental assessment philosophy and therefore is not an alternative to either approach. Similarly, *a priori* judgments based on process chemistry, thermodynamics, etc. are not acceptable practices in this context.

Since both the direct and phased approaches offer, at least in principle, equal promise for ultimate success (i.e., comprehensiveness and complete characterization), it is worthwhile to examine their relative resource requirements. Several studies were conducted with the objective of comparing the costs of direct and phased (with elimination of low priority streams) sampling and analysis approaches. *(2,3)* A number of processes were evaluated during these studies and the results for two unit operations — a limestone wet scrubber and full-scale low-Btu coal gasifier — are taken as examples. The scrubber involved seven feed or waste stream sampling sites. The gasifier contained 70 identifiable stream sampling points. The total estimated costs for both processes by both approaches are shown in Table I.

Table I

Estimated Total Costs of Direct vs Phased Approaches to Sampling and Analysis

Process	Phased	Direct
Limestone Wet Scrubber	$350,000	$ 500,000
Coal Gasifier	$725,000	$1,450,000

In both bases, the phased approach was found to be more cost effective than the direct approach even though the scrubber and coal gasifier differ markedly in size, complexity, basic technology, and total cost of sampling and analysis. The cost advantages of the phased sampling and analysis approach were found to be approximately proportional to the complexity of the process being sampled. Within the phased approach, the initial sampling and analysis costs were shown to be 10 percent of the total cost of the phased effort. Thus, many qualitative judgments, including whether or not a full-scale endeavor is at all necessary, can be made at low cost before a commitment is made to initiate a detailed assessment.

This actual resource savings is only one aspect of justification for the phased scheme. As the result of information developed in the survey phase, a significant improvement in sampling accuracy and completeness can be anticipated during later phases. It is very doubtful that equal data could actually be acquired in a direct approach due to the lack of the very necessary learning processes involved in difficult source sampling and analytical projects.

As the result of these studies, the phased approach was selected for further development and implementation. The strategy makes use of the three levels of sampling and analysis mentioned earlier. The survey phase is defined as Level 1; the detailed analysis of priority components, Level 2; and the monitoring of selected components, Level 3.

Sampling Programs in a Phased Approach

It has been noted that it is not sound practice to attempt to define a detailed sampling program until: (1) the general characteristics of the streams in question have been evaluated, and (2) the nature of any unfavorable sampling system/sample interactions has been considered (e.g., chemical reaction, volatility loss). Hence, an effective sampling program involves a series of reiterative tests in which each iteration enhances the source assessment by focusing resources and efforts on the pollutants and streams of concern and improves the accuracy of the sampling program.

Level 1 sampling stresses the concept of completeness by presuming that all streams leaving the process will be sampled. Level 1 sampling is not predicated on *a priori* judgments as to stream composition. The techniques utilized presume that whatever knowledge is available is, at best, incomplete. Predictive and extrapolative techniques employed during source assessments serve as a check on the empirical data and not as a replacement for them. Level 1 sampling systems are therefore envisioned to permit collection of all substances in the stream at a reasonably high level of efficiency. They do not necessarily produce information as to specific substances or their chemical form. Further, Level 1 sampling programs are designed to make maximum use of existing stream access sites. While some care must be exercised to ensure that the samples are not strongly biased, the commonly applied concepts of multiple point, isokinetic, or flow proportional sampling are not rigidly adhered to. Normally, the sample is collected over one full cycle of each desired set of process operating conditions. When a series of discrete samples result, they are combined to produce a single "average" value for the total process cycle.

Level 2 sampling programs are directed toward a more detailed representation of stream composition. They are not as "inclusive" as Level 1, in that resources are expended to improve information only on streams of a critical nature and on compound classes defined as present by Level 1 analysis. Level 2 sampling is optimized for specific compounds or classes of compounds contained in the streams sampled. Level 2 also provides a more quantitative description of the concentrations and mass flow rates of the various substances in the stream. Further, recommended procedures for compliance testing should be introduced into the program to ensure that the data acquired by the procedures selected for Level 2 sampling can be correlated with regulatory requirements.

One primary refinement will be the need for more rigorous attention to selection and preparation of sampling sites. Additionally, adherence to procedures for acquiring a representative sample must be incorporated into the test procedures. Level 2 sampling should also provide for replication of samples in order to further improve accuracy and be more representative. In many cases, Level 2 sampling will require not only more care in use but also modifications of Level 1 equipment and/or the application of entirely new sampling methods. Such cases result from the necessity to more definitively identify the materials which produce the adverse environmental problems. For example, if Level 1 has indicated a high concentration of sulfur-containing spe-

cies, Level 2 sampling must be specifically designed to isolate the sulfur-containing materials into appropriate fractions which can be analyzed for individual compounds or compound classes.

At Level 3, emphasis is placed on the variability of stream composition with time and process or control system parameters. When it has been determined at Level 1 that a stream is environmentally unacceptable and at Level 2 what the unacceptable components are, it is necessary to accurately define the range of values to be expected and the effectiveness of a control process if control equipment is installed. An effective Level 3 sampling program is designed to monitor a limited number of selected compounds or compound classes. Since Level 3 sampling is designed to provide information over a long period of time the sampling procedures must be carefully planned to minimize costs. Such programs must be tailored to the specific requirements of each stream being monitored. Based on the information developed at Level 2, specialized sampling procedures can be designed to track key indicator materials at frequent intervals. If at all possible, Level 3 should incorporate continuous monitors where appropriate.

During Level 3 programs, it is anticipated that Level 2 sampling will be conducted at predetermined intervals to check the limited Level 3 information. Further, recommended procedures for compliance testing should continue to be applied in the program to ensure that data correlations with regulatory requirements can be met on a long-term basis.

Analytical Methodology in a Phased Approach

During an environmental source assessment, the analytical methods applied will vary from relatively simple, manual wet chemistry to highly complex instrumental techniques. Analyses proceed from general, broadly applicable survey methods to more specialized techniques tailored to specific component measurements. This very broad range requirement has been structured to adhere to the same level concept described for the sampling program. At each phase of the analytical program, the depth and sophistication of the techniques are designed to be commensurate with the quality of the samples taken and the information required. Hence, expenditure of analytical resources on screening samples from streams of unknown pollution potential is minimized.

Level 1 sampling provides a single set of samples acquired to represent the average composition of each stream. This sample set is separated, either in the field or in the laboratory, into solid, liquid, and gas-phase components. Each fraction is evaluated with survey techniques which define its basic physical, chemical, and biological characteristics. The survey methods selected are compatible with a very broad spectrum of materials and have sufficient sensitivity to ensure a high probability of detecting environmental problems. Analytical techniques and instrumentation have been kept as simple as possible in order to provide an effective level of information at minimum cost. Each individual piece of data developed adds a relevant point to the overall evaluation. Conversely, since the information from a given analysis is limited, all the tests must be performed to provide a valid assessment of the sample.

Physical analysis of solid samples is incorporated into Level 1 because the size and shape of the particles have a major effect on their behavior in process streams, control equipment, atmospheric dispersion, and the respiratory system. In addition, some materials have characteristic physical forms which can aid in their identification.

Chemical analyses which determine the types of substances present, are incorporated to provide information for predicting control approaches, atmospheric dispersion/-transformation, and potential toxicity of the stream. Finally, because prediction of hazard based on physical and chemical analyses alone is subject to many uncertainties, biological assay techniques are incorporated as a measure of the potential toxicity. The basic Level 1 analytical procedures are given in Table II.

Table II

Basic Level 1 Analyses

Physical:	Cyclone particle size
	Optical microscopy
Chemical:	Spark source mass spectormetry
	Wet chemical (selected anions)
	Gas chromatography
	Liquid chromatography
	Infrared spectrometry
	Low resolution mass spectrometry
Biological:	Rodent acute toxicity
	Microbial mutagenesis
	Cytotoxicity
	Fish acute toxicity
	Algal bioassay
	Soil microcosm
	Plant stress ethylene

The analytical procedures applied at Level 2 may be extensions of the Level 1 procedures. In most cases, however, information developed at Level 1 will provide background for selection and utilization of more sophisticated sampling and analysis techniques. Because Level 2 analyses must positively identify the materials in sources which have already been found to cause adverse environmental effects, these analyses are the most critical of all three levels. It is equally important, however, that the analyses be conducted in an information-effective manner. This is because increasing specificity and accuracy result in cost escalations which are, at best, exponential rather than proportional. Due to the multiplicity of analytical techniques required and the potential for unnecessarily high expenditures, the analyses must be conducted with a full awareness of the information requirements of the environmental assessment program.

It is evident from the preceding comments that Level 2 analyses cannot be conducted via a prescribed series of tests. Each sample will require the analyst to select appropriate techniques based on the information developed in Level 1 and the information required for the assessments. Needless to say, this will encompass at one time or another virtually all the tools available to the analytical chemist and biologist, and a great deal of skill in their application. Of major importance will be the use of separation schemes for isolating fractions since the interpretation of both chemical and biological data from complex samples is a difficult, if not impossible, task. As with Level 2 sampling, the analytical scheme should incorporate the chemical and biological tests required by regulatory agencies.

The analytical procedures for Level 3 are specific to selected components identified by Level 2 analysis and are oriented toward determining the time variation in the concentrations of key indicator materials. In general, the analysis will be optimized to a specific set of stream conditions and will therefore not be as complex or expensive as the Level 2 methods. Both manual and instrumental techniques may be used, provided they can be implemented at the process site. Continuous monitors for selected pollutants should be incorporated in the analysis program as an aid in interpreting the data acquired through manual techniques. The total Level 3 analysis program should also include the use of Level 2 analysis at selected intervals as a check on the validity of the key indicator materials which reflect process variability.

Discussion

The major emphasis in environmental measurements over the past 2 years has been on development of procedures for Level 1. As presently conceived, Level 1 is structured to produce a cost-effective information base for prioritizing streams and for planning any subsequent programs. The specific procedures applied are detailed in two published manuals, the first covering sampling and chemical analysis *(4)* and the second biological tests *(5)*. Application of the complete battery of procedures provides input data to support evaluation of the following questions:

a. Do streams leaving the processing unit have a finite probability of exceeding existing or future air, water, or solid waste standards or criteria?

b. Do any of the streams leaving the processing unit contain any classes of substances that are known or suspected to have adverse environmental effects?

c. Into what general categories (classes) do these substances fall?

d. What are the most probable sources of these substances?

e. Based on their adverse effects and mass output rates, what is the priority ranking of streams?

f. For streams exhibiting potential adverse environmental effects, what is the basic direction that control strategies are likely to follow?

The overall accuracy goal of Level 1 is to report the true value within a factor of 3. This means that a reported value between 30 and 300 is acceptable when the true value is 100. Many of the Level 1 sampling and analysis techniques are more accurate than this goal, but the relaxation of traditional limits allows significant cost savings. In general, grab sampling procedures are utilized for solid and liquid samples in order to minimize sampling costs.

In the case of particulate laden stack gases it is necessary to use sophisticated and relatively expensive equipment to collect valid samples, even at Level 1. To provide this type of unbiased sampling, the acquisition of gas samples requires the use of a sampling train designed specifically for environmental assessment sampling. The Source Assessment Sampling System (SASS) *(6)* has been designed to operate at 150 1pm and collect both solids and vapors. The entrained particulates are fractionated into four sizes: $> 10\mu m$, 3-10 μm, 1-3 μm, and $< 1\ \mu m$. Vapor-phase organic materials are adsorbed on a solid sorbent (XAD-2), and the inorganic vapors are retained in the chemically active impinger solutions. Because it is impossible to predict the concentration of a constituent in the gas stream at the start, sampling is based on the minimum

volume of gas necessary to provide detection of materials in the analytical scheme. A minimum of 30 m^3 (1000 ft^3) is sufficient to ensure detection of materials in the source at 1 mg/m^3 (approximately 1 $\mu g/m^3$ in the receiving media). The overall process scheme for samples from this system is shown in Figure 2.

Sampling of fugitive air emissions presents problems similar to those of stack gases and specialized equipment is also necessary for this operation. A Fugitive Assessment Sampling Train (FAST) has been designed which operates at 5.2 m^3/min. Entrained particles are fractionated into > 15μm, 3-15 μm, and < 3 μm and organic vapors from a side stream are trapped in an XAD-2 sorbent trap.

An overview of the Level 1 chemical analysis scheme is shown in Figure 3. If divided along classical lines of inorganic and organic analysis, it can be seen that the primary techniques applied for inorganic analysis are gas chromatography for the gaseous components and spark source mass spectrometry (SSMS) for elemental analysis of solids and liquids. A number of anions including sulfate, nitrate, and phosphate are presently analyzed by wet chemical techniques. However, future analysis will be based on ion chromatography to increase the number of anions detectable. Atomic absorption has been applied only for mercury, arsenic, and antimony which were thought to be lost by vaporization during SSMS analysis. Recent data indicates that SSMS values for arsenic are within Level 1 accuracy requirements and that antimony values may also be acceptable. It is probable that AA will be retained in future schemes only for mercury analysis. Further development is also necessary to improve the comprehensiveness of inorganic gas analysis.

The Level 1 organic analysis strategy employs four analytical operations in the control scheme. Gas chromatography is applied at the sampling site to analyze for organic substances with boiling points below 100°C. The separation is essentially by boiling point with flame ionization detection. Column conditions are such that individual compound separation is not achieved — the desired goal being to group all materials into seven boiling point ranges.

In the laboratory conducted portion of the organic analysis, a seven step liquid elution chromatography separation on silica gel forms the central part of the scheme. It is an analytical step (in that behavior of a given class of compounds is predictable) as well as a separation step (since the fractions may be further analyzed much more readily than the original mixture). The behavior of selected classes of compounds with respect to the chromatographic conditions employed is shown in Figure 4.

The second laboratory operation is determined of the total organic content. This operation allows quantitation of the organics in each of the chromatographic fractions as well as aliquot size selection for optimum column operation. The original Level 1 scheme depended entirely upon reduction to dryness and weighing for total organics determination. Recent data show that many materials in the boiling range below 275°C may be partially lost by that approach. Accordingly, a gas chromatographic procedure for volatile organics has been adopted as a part of the Level 1 strategy. Total organic content is obtained by addition of the gravimetric results and the total chromatographable organics (TCO).

The third analysis is by infrared absorption spectrophotometry. This classical technique is often overlooked in today's mass-spectrometry dominated laboratory, but still remains a powerful tool which provides considerable information at moderate cost. Infrared spectra of the seven chromatographic fractions may be used to confirm

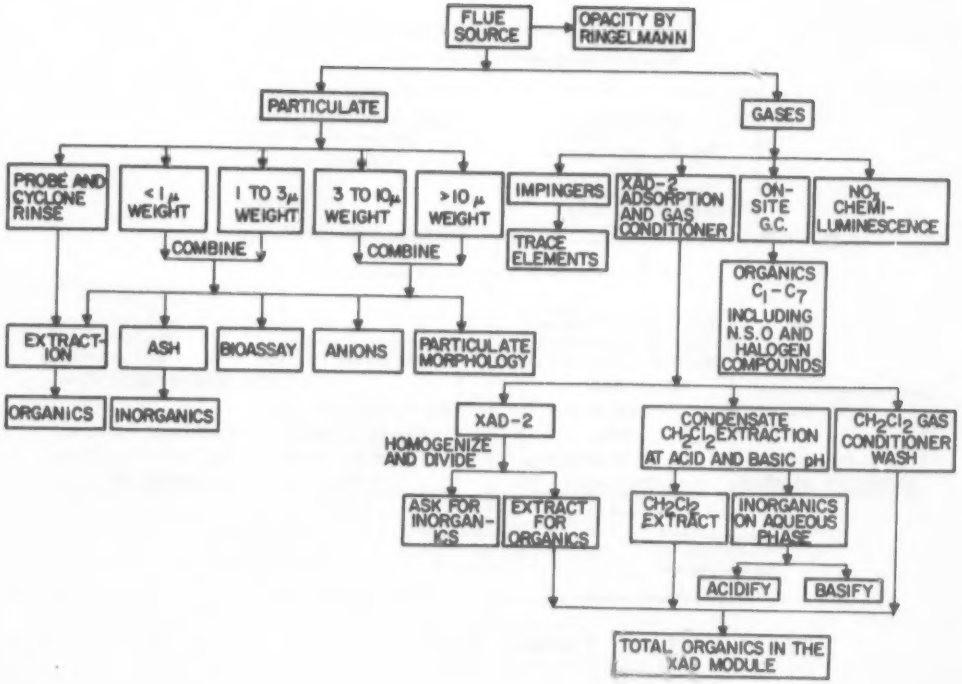

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Figure 2. Flue gas sampling flow diagram (2)

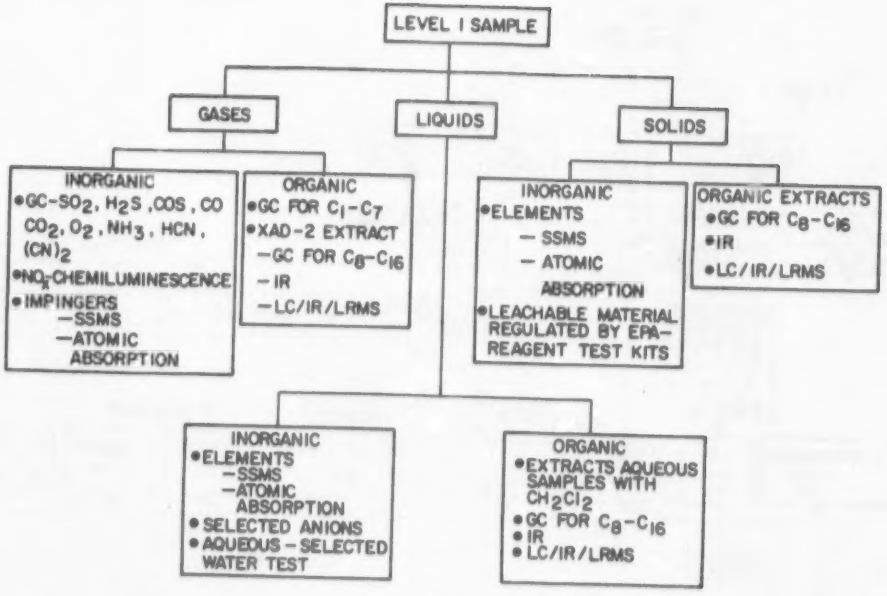

Figure 3. Multimedia analysis overview (2)

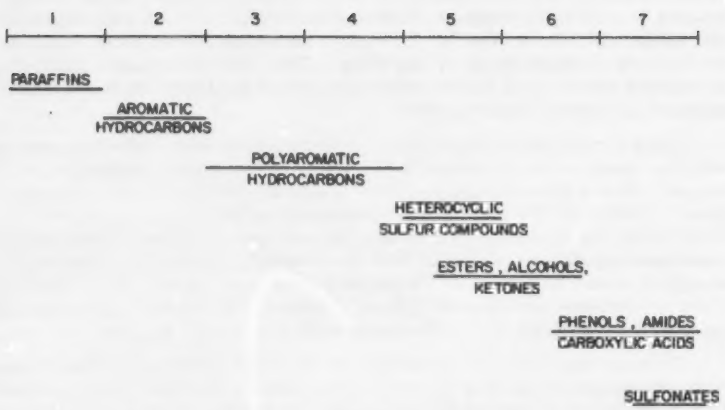

Figure 4. Liquid chromatographic fractions vs. class types

the presence or absence of compound classes or functional groups as indicated by the chromatographic data. It is occasionally possible to identify specific compounds from the infrared spectra but, as previously mentioned, the complexity of most environmental samples makes this the exception rather than the rule.

Finally, low resolution mass spectrometry (LRMS) is applied to each separation fraction which exceeds a specified concentration when referred to the sample sources. The present levels are 0.5 $\mu g/m^3$ for gas streams, 1 mg/kg for solids, and 0.1 mg/1 for liquids. The selection of this particular technique, firmly in the middle of a transition between Levels 1 and 2, caused many philosophical problems concerning its proper use. The original Level 1 scheme did not contain LRMS. It has been included in the modified strategy to prevent potential triggering of Level 2 efforts based on large amounts of suspicious, but innocuous, organics. However, LRMS can be costly if constraints are not placed on how frequently it is applied.

Biological tests are incorporated in Level 1 because physical and chemical analysis cannot provide a reliable measure of the potential biological response to complex samples. In addition, bioassays can detect complex biological effects such as synergism and antagonism. On the other hand, bioassays cannot identify the cause of toxicity or mutagenicity or suggest means of controlling it. Thus, physical, chemical, and biological analyses must be used to complement one another at all three levels of the phased approach to environmental assessment.

Level 1 biological testing is limited to whole sample testing which is consistent with the survey nature of this level. The testing of fractionated samples or specific components of a given sample involves a degree of specificity more appropriate to Level 2 testing. The bioassays include assessments of both health and ecological effects. Health effects tests estimate the potential mutagenicity, potential or presumptive carcinogenicity, and potential toxicity of the samples to mammalian organisms. The ecological effects tests focus on the potential toxicity of the samples to vertebrates (fish), invertebrates, and plants in freshwater, marine, and terrestrial ecosystems. Figure 5 shows the overall biological scheme applied to Level 1 samples.

Three primary tests are incorporated in the health effects area. The microbial mutagenesis assay is based on the property of selected *Salmonella typhimurium* mutants to revert from a histidine requiring state to prototrophy due to exposre to various classes of mutagens. The test can detect nanogram quantities of mutagens and has been adapted to mimic some mammalian metabolic processes by the addition of a mammalian liver microsomal fraction. The test is used as a primary screen to determine the mutagenic activity of complex mixtures or component fractions.

Cytotoxicity assays employ mammalian cells in culture to measure cellular metabolic impairment and death resulting from exposure *in vitro* to soluble and particulate toxicants. Mammalian cells derived from various tissues and organs can be maintained as short term primary cultures or, in some cases, as continuous cell strains or lines. The cytotoxicity assays, incorporated as part of Level 1 analysis, employ primary cultures of rabbit alveolar (lung) macrophages (RAM) and maintenance cultures of strain WI-38 human lung fibroblasts.

The third health effect bioassay employed utilizes acute toxicity in whole animals (rats). Since the major objective of the Level 1 biological testing procedure is to identify toxicology problems at minimal cost, a two-step approach is taken to the initial acute *in vivo* toxicology evaluation of unknown compounds. The first is based on a

Figure 5. Biological analysis overview (5)

quantal (all-or-none) response and the second on a quantitative (graded) response. Normally, the quantal test is used to determine the necessity to carry out the quantitative assay. In the quantal test, a single dose of 10 g/kg body weight of the sample being evaluated is administered to 10 rats and their behavior observed for 14 days. If no mortality occurs, additional tests are not conducted. If the administration of the sample causes a single death, a quantitative study on 80 animals is conducted at various dilutions of the sample.

There are also three primary tests applied to aquatic assays of water effluents. The same basic tests are used for both fresh water and marine assays; the primary variation is in the species selected. An algal assay is based on the principle that growth is limited by the nutrient that is present in shortest supply with respect to the needs of the organism. The test is designed to be used to quantify the biological response (algal growth alteration) to changes in concentrations of nutrients and to determine whether or not various effluents are stimulative or inhibitory to algal growth. Measurements are made by adding a selected test alga to test water containing the sample and determining algal growth rates at appropriate intervals.

Acute static bioassays are employed to evaluate sample effects on fish and microinvertebrates. Fathead minnows and *Daphnia pulex* are the freshwater species employed, while sheepshead minnows and grass shrimp are used for marine assays. In all cases, the test organisms are exposed for 96 hours to prescribed concentrations of the sample introduced into holding tanks maintained at the same environmental conditions as a control population.

Two bioassays are employed to evaluate the effect of samples on terrestrial life forms. For gas samples, the plant stress ethylene test is presently recommended. This test is based on the well-known plant response to environmental stress: release of elevated levels of ethylene (under normal conditions plants produce low levels of ethylene). The test is designed to expose plants to various levels of gaseous effluents under controlled conditions. The ethylene released during a set time period is then measured by gas chromatography to determine toxicity of the effluent. For liquid and solid samples, a soil microcosm test is employed. The sample is introduced on the surface of a 5 cm diameter by 5 cm deep plug of soil obtained from a representative ecosystem. Evolution of carbon dioxide, transport of calcium, and dissolved oxygen content of the leachate are the primary quantifying parameters.

Results

All the elements in the Level 1 scheme have been utilized in studies of discharges from industrial and energy processes. The data developed is far too voluminous to be presented here and the results discussed are, therefore, more a demonstration of the utility and viability of selected elements within the scheme. It should also be noted that all the data presented was acquired to evaluate the Level 1 methodology and should *not* be interpreted as indicative of emissions from the processes studied.

In a study of the precision of the SASS train for the collection of particulates and organics from gas streams, total particulate loadings determined with two independent SASS trains agreed within 20 percent of the value determined with a standard EPA Method 5 train operated simultaneously on triplicate runs. The size distributions determined by the two trains were also in good agreement for all three runs as illustrated in Figure 6. The quantity and distribution of extractable organics between the two vstems was also well within Level 1 tolerances as shown in Table III.

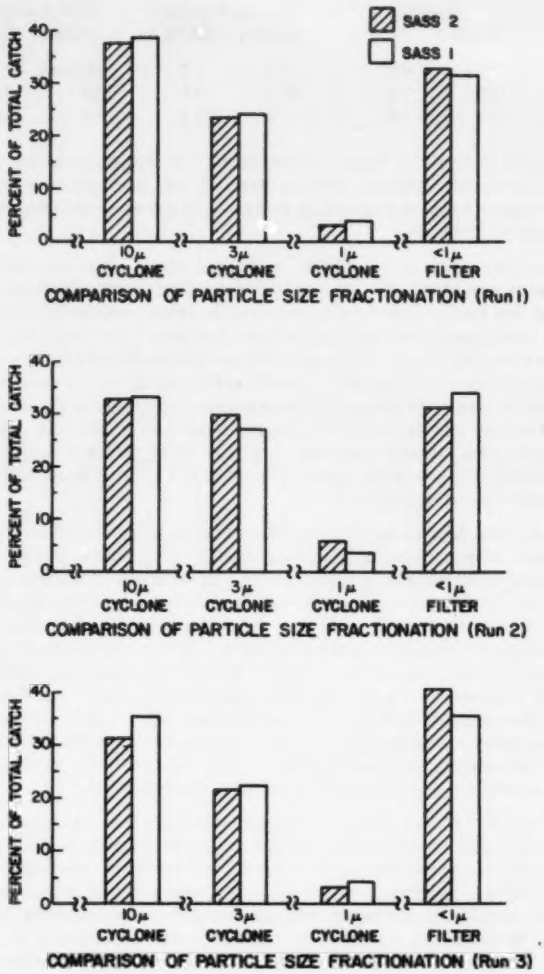

Figure 6. Comparison of particle size fractionation of two SASS trains

Table III
Organic Extractables (mg/m³)

	Cyclone		XAD-2 (Extract)		XAD-2 (Module)	
	SASS-1	SASS-2	SASS-1	SASS-2	SASS-1	SASS-2
TCO	0.03	0.01	3.4	3.6	(Rinse)	
Grav	1.6	1.6	10.2	9.0	69	81
Total	1.7	1.6	13.6	12.6	69	81

Additional analysis of these samples using the liquid chromatographic separation, total chromatographable organics, infrared, and low resolution mass spectrometry demonstrated that the sampling and analysis scheme produced reproducible data as shown in Table IV.

The samples acquired from these tests were also used to evaluate inter- and intra-laboratory precision for the various elements of the anaytical scheme. In general, it was found that the analysis for total extractable orgaic content and the distribution between chromatographable and gravimetric fractions were much better than the factor of 3 required by Level 1. Triplicate analysis by four laboratories gave an average total organic content of 480 mg and a coefficient of variation of 4 percent. However, the results of the liquid chromatographic separation indicated a wider range of values in the distributions by fractions, indicating a need for more carefully controlled column preparation and sample handling. A typical set of values is shown in Table V. (This and subsequent data was acquired with an eight fraction scheme which has since been reduced to seven fractions.)

Tests of a coal fired power plant and an oil fired boiler show the ability of Level 1 to discriminate between process operating conditions. In Figure 7, the cross hatched bars represent the distribution of organics under conditions producing maximum operating temperatures. Under these conditions, the maximum weight of organic emissions was found in fraction 5, with generally much smaller concentrations in all other fractions. With water injection on the oil fired unit and reduced load on the coal fired unit, the organics show a much more complex distribution with significant increases of materials in fractions 2, 3, and 7. In both cases, the concentration of total organics detected in the emissions by the Level 1 analyses was found to increase by a factor of 2 under the conditions producing lower operating temperatures. While these results do not identify the specific compounds present, they show the magnitude of the change and the classes of compounds which warrant further analysis.

An indication of the utility of bioassay procedures in the Level 1 scheme is available from a study performed on the particulate collected from 10 industrial process streams prior to control devices (7). An initial cytotoxicity screening of the samples was performed at a particulate concentration of 1000 μg/ml of culture medium containing rabbit aveolar macrophages. Samples found in the initial screening to produce cell deaths greater than 15 percent were retested at concentrations of 1000 μg/ml, 300 μg/ml, and 100 μg/ml of culture medium. In addition, an attempt was made to ascertain whether the toxicity of a given particulate sample was due to the particles themselves and/or soluble component(s) released into the medium. The particulate matter was incubated in the culture medium (less serum but including antibiotics) for 20 hours and then removed from the medium via centrifugation and filtration through a 0.22 μm Millipore filter. The filtered supernatant and centrifuged particles (resuspended in

TABLE IV. Organic Categories in SASS Samples

Categories	Concentration (mg/m³) SASS-1	SASS-2
Aliphatic hydrocarbons	1.1	1.1
Halogenated aromatic HC's	–	–
Aromatic HC's-benzene	0.6	0.1
<216	28.7	28.2
>216	25.6	28.7
Heterocyclic N	20.1	24.0
Heterocyclic S	2.4	2.5
Heterocyclic O	2.2	6.7
Phenols	0.2	0.3
Esters	0.5	0.2
Ethers	–	–
Amines	–	–
Amides	–	–
Carboxylic acids	0.6	0.7
Sulfonic acids, sulfoxides	–	–
Sulfur	0.2	0.7
Inorganics	0.1	–
Unclassified	0.3	1
• Silicones	0.1	–

TABLE V. TCO/GRAV Results: Field Sample, XAD-2 Extract, Run 1 (mg)

Fraction	TCO				GRAV				Total			
	A	B	C	D	A	B	C	D	A	B	C	D
LC1	1.4	<0.4	12.0	2.1	11.5	4.0	4.8	—	13	4	17	2
LC2	15.2	<0.4	60.3	120	4.6	6.4	84.2	200	20	7	145	320
LC3	54.7	31	40.3	2.6	259.4	284	177.6	19	314	315	218	22
LC4	0.5	2.3	9.2	1.4	10.1	22	12.8	—	11	24	22	1
LC5	0.9	0.84	0.4	7.4	31.3	8.8	7.6	—	32	10	8	7
LC6	3.2	1.0	18.4	13	16.6	38	27.1	110	20	39	46	123
LC7	0.5	<0.4	21.6	1.9	2.8	23	3.6	—	3	23	25	2
LC8	0.9	<0.4	N.R.	8.3	3.7	37	0	50	5	37	0	58
TOTAL	77.3	36.7	162.2	156.7	340	423.2	317.7	379	418	459	481	535

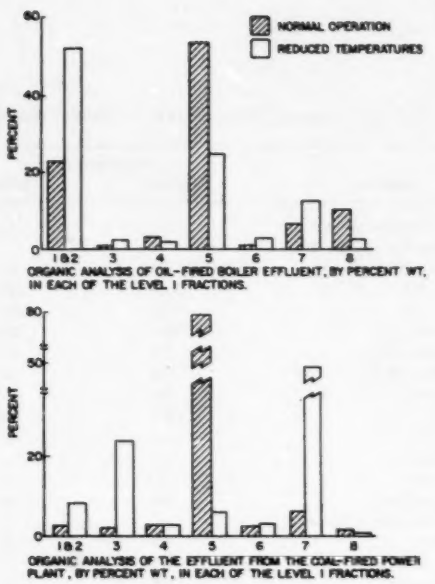

Figure 7. Effect of process variables on organic weights in Level 1 fractions

TABLE VI. Viability of Rabbit Alveolar Macrophages Exposed to Sub-Micron Particle Filters

Filter Sample	Total Sample	Supernatant	Dried Filter
Oil Fired Power Plant (< 3μm)	20.4[a]	10.5[a]	30.1[a]
Copper Smelter (< 3μm)	26.3	29.5	41.0
Aluminum Smelter (< 3μm)	28.2	24.9	86.3
Aluminum Smelter (> 3μm)	31.5	32.1	60.8
Iron Sintering (< 3μm)	33.0	55.2	95.7
Copper Smelter (> 3μm)	37.2	30.6	35.6
Iron Sintering (> 3μm)	56.1	58.8	99.5
Paper Mill (< 3μm)	56.1	76.7	97.9
Sludge Incinerator (< 3μm)	92.1	71.8	93.8
Ceramics Plant (< 3μm)	93.0	53.6	98.4
Open Hearth Furnace (Total)	95.9	98.8	97.4
Coke Oven Heaters (< 3μm)	97.6	98.8	99.6
Basic Oxygen Furnace (Total)	98.3	98.4	99.6
Teflon Control Filter	Non-Toxic	Non-Toxic	Non-Toxic

[a]Percent viable cells (mean of two observations)

fresh medium) were then independently tested for cytotoxicity. Table VI is a tabulation of the viability (percent living cells) of the samples tested. The sources have been ranked on a relative basis of toxicity of the total sample. Except for the aluminum smelter samples, the finer particulate (< 3 μm) is more toxic than the larger (> 3 μm). Comparing the second and third columns (Supernatant and Dried Filter) indicate that the leachable components (supernatant) were usually responsible for the observed toxicity. In the case of the oil fired power plant and copper smelter samples, however, the undissolved particulate retained a significant level of toxicity.

Conclusions

The phased approach developed for environmental assessments has been successfully implemented on a number of programs. The Level 1 results have been useful for defining potential problems for further study and directing additional resources into the areas of greatest need. While not all the elements of the scheme have been found effective on each study, every element has produced needed data in at least one or more of the individual studies. In considering the utility of the approach it is therefore necessary to consider the overall results rather than the value of any single component.

The procedures selected initially have been constantly improved in detail; however, no significant changes in the basic techniques have been necessary. The phased approach is, therefore, a viable and cost effective concept for identifying potential environmental problems associated with discharge from industrial and energy processes.

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The people making significant contributions to the development of the phased approach are too numerous to list here. We trust that they, as well as the reader, will recognize that this paper would not have been possible without their efforts.

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